

Research Article

Enhanced Colouration Efficiency of Pulsed DC Magnetron Sputtered WO₃ Films Cycled in H₂SO₄ Electrolyte Solution

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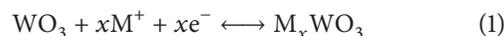
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In the present investigation, we report on DC power and pulsing frequency induced changes in electrochromic properties of pulsed DC magnetron sputtered WO₃ films by intercalating/deintercalating H⁺ ions from 0.1M H₂SO₄ electrolyte solution. The observed efficient colouration ↔ bleaching mechanism of WO₃ films confirms the effective electrochromic nature of the films associated with the electrochemical intercalation/deintercalation of H⁺ ions and electrons into WO₃ lattice. The higher optical modulation was observed in the visible region of the optical transmittance spectra of colored and bleached WO₃ films. The maximum coloration efficiency of 79 cm²/C was observed the first time for the film deposited at a DC power of 150 W and a pulsing frequency of 25 kHz.

1. Introduction

Nowadays, electrochromism is much exploited in commercial automotive markets for regulating the amount of radiation passing through the electrochromic mirrors which are electronically tinted or darkened to reduce the headlight glare [1]. Electrochromism is nothing but exhibiting a change in transmittance when a small potential is applied. It is well known that transition metal oxides exhibit excellent metal-insulator transition behavior and possess electrochromic property. Among the transition metal oxides, tungsten oxide (WO₃), an n-type cathodic electrochromic material having empty perovskite type of structure, has been recognized and studied as a promising candidate for electrochromic device and smart window applications due to its high coloration efficiency and better electrochemical stability [1]. Thin WO₃ film is visibly colorless or transparent in its oxidized state, that is, in W⁶⁺ state, and turns into blue color when it is reduced to W⁵⁺ state by applying a negative potential and this property can be reversed back by applying positive potential. This phenomenon can be facilitated when electrons and metal ions M⁺ (M = H, Li, Na, or K) are intercalated or deintercalated and the electronic structure of WO₃ is modified by the upward

shift of the Fermi level. Thus, the optical property of WO₃ films transforms from transparent to an absorbing nature due to the filling of t_{2g} band of perovskite structure by the excess electrons [2]. This can be explained by the following reaction:



In general, the colouration of electrochromic WO₃ films can be explained by the following aspects: electronic transitions between W⁵⁺ and W⁶⁺ ions [3], colour center formation at the oxygen vacancies [4], small polaron absorption [5], intraband transitions [6], and conduction band splitting in the presence of injected electrons and electronic transitions between the formed subbands [7]. It is well recognized that the performance of an electrochromic device depends strongly on the overall material morphology, microstructure, and crystallinity, which are in turn related to the technique used for the preparation of active electrochromic electrode thin film. Hence, establishing optimum parameters or a special technique for WO₃ thin film preparation may permit getting specific microstructures that are suitable for electrochromic device application [8].

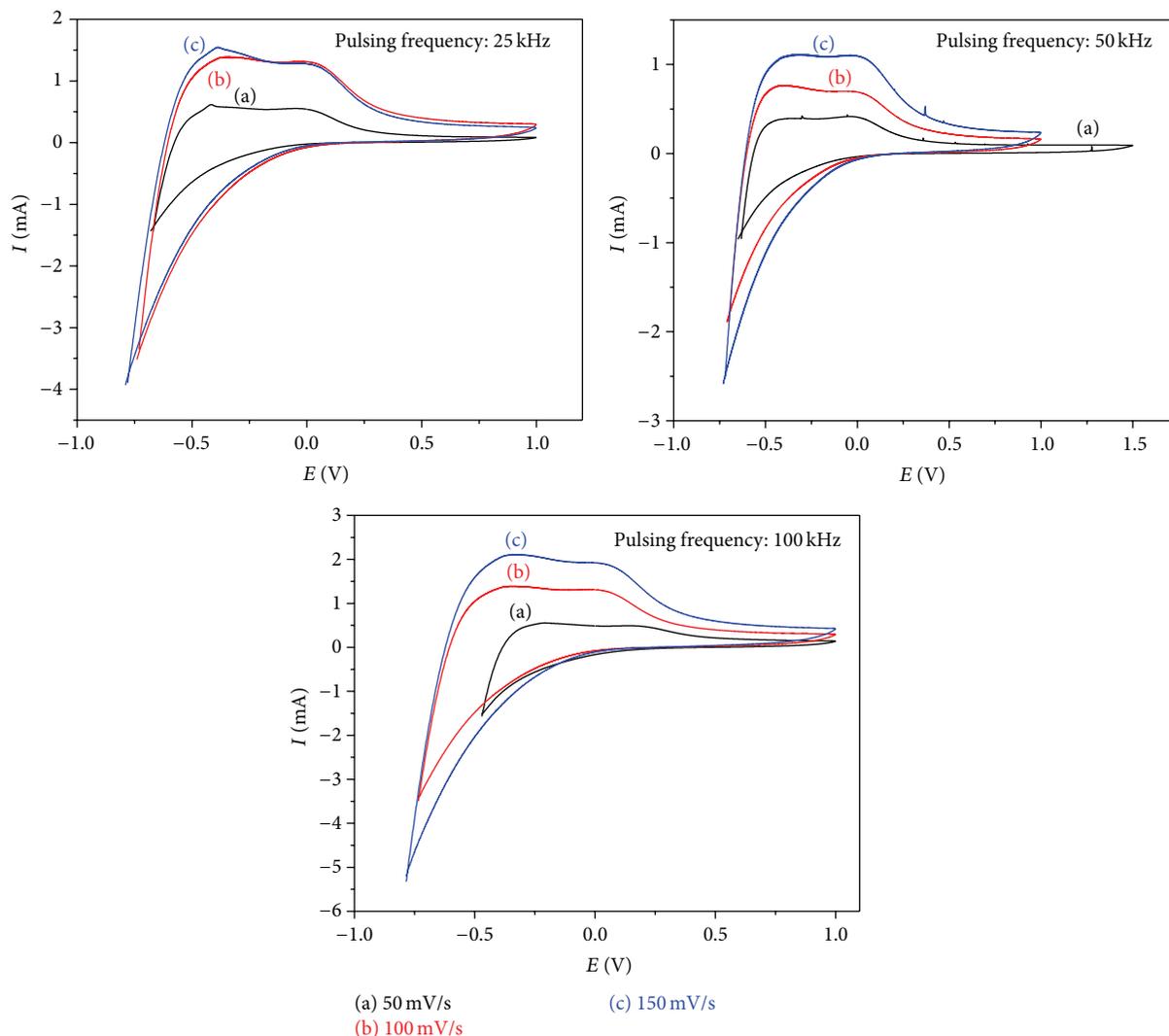


FIGURE 1: Pulsing frequency induced change in cyclic voltammograms of WO_3 films deposited at 50 W DC power and cycled in 0.1 M H_2SO_4 electrolyte solution with various scan rates.

WO_3 thin film can be prepared by a wide number of techniques such as electrodeposition [9], spray pyrolysis [10], conventional DC sputtering [11], electron beam evaporation [12], and thermal evaporation [13]. In addition, WO_3 thin films were grown by chemical vapor deposition (CVD) method using tungsten hexacarbonyl and WF_6 precursor solutions [14, 15]. Nagata et al. [16] have also prepared WO_3 films by rf magnetron sputtering using a tungsten metal target. Among them, conventional DC sputtering has been considered a well-established technique and largely used for the deposition of thin films. However, during WO_3 film deposition by using DC magnetron sputtering an electrically insulating layer is built up on the surface of the target which leads to arcing due to charge accumulation. In this case, the WO_3 target is fused and only sputtered within a small region of the target surface; hence defects in the deposited layer are likely to be created [17]. This problem can be overcome by using pulsed DC sputtering since the accumulated charge of insulating layers is neutralized easily during the change in polarity of a pulse

and thereby the reduction in the arcing event. It consequently prevents deterioration of film properties and the deposition process also remains stable [17]. Thus, the defect-free WO_3 thin films with superior uniformity, quality, and specific microstructure can be deposited by pulsed DC magnetron sputtering. However, to date, very few reports are available on the preparation of WO_3 thin films by pulsed DC magnetron sputtering technique [18]. In the present investigation, we report the effects of pulsing frequency and DC power on electrochromic property of WO_3 thin films prepared by pulsed DC magnetron sputtering. Various electrochemical parameters of WO_3 films were evaluated and discussed in light of available reports.

2. Experimental

Thin films of tungsten oxide (WO_3) were deposited by pulsed DC magnetron sputtering technique (Advanced Energy Pinnacle Plus Pulsed DC Power Supply) using WO_3 target.

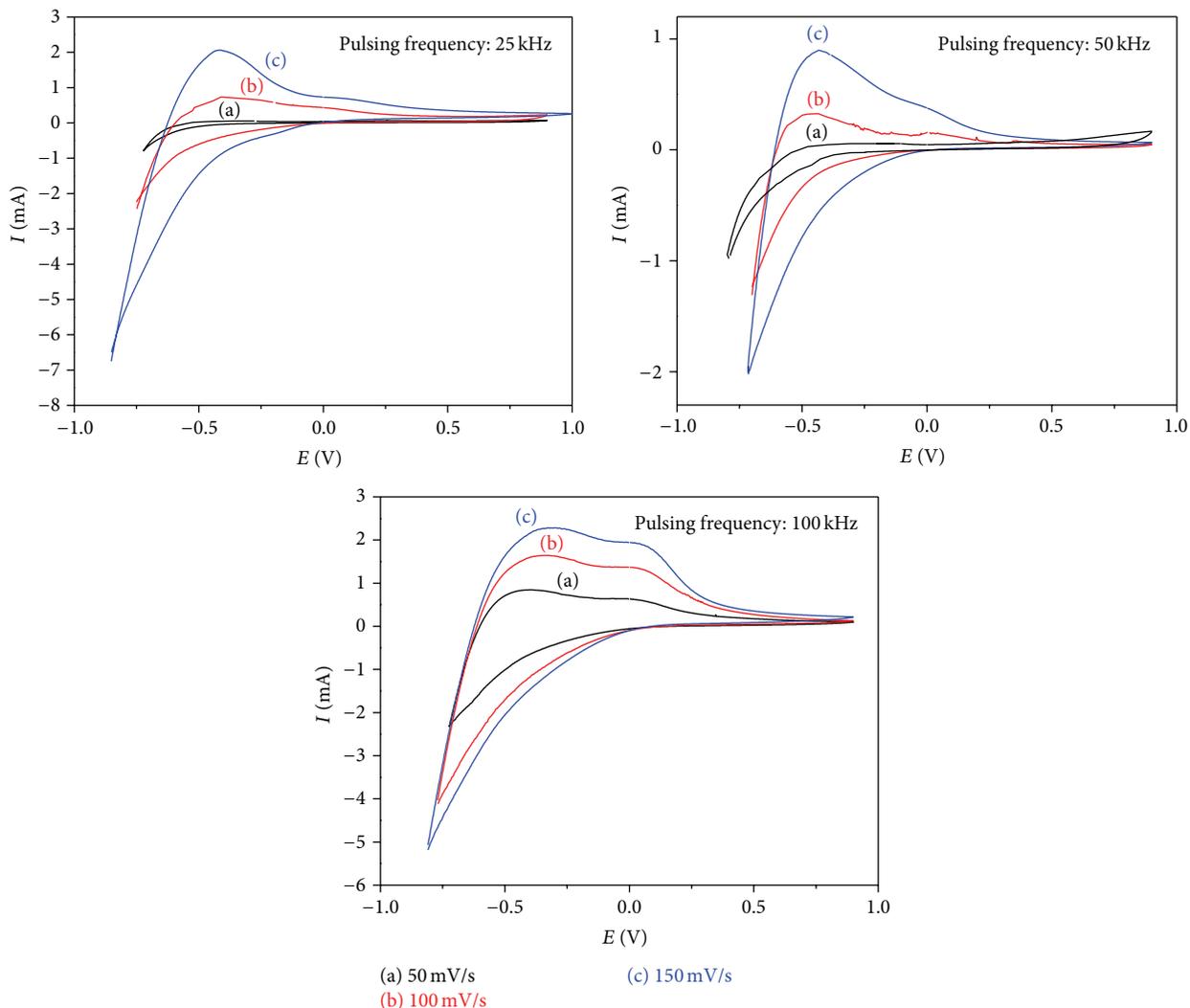


FIGURE 2: Pulsing frequency induced change in cyclic voltammograms of WO_3 films deposited at 100 W DC power and cycled in 0.1 M H_2SO_4 electrolyte solution with various scan rates.

Powder of tungsten oxide (Aldrich; 99.999% purity) was uniaxially pressed at 20 MPa (2 inch dia.; 5 mm thick) and sintered at 1000°C for 8 hrs. The sintered WO_3 pellet was used as a target to deposit thin WO_3 films on pre-cleaned fluorine doped tin oxide ($\text{SnO}_2:\text{F}$) coated glass substrate. The distance between the target and the substrate was kept fixed at 9 cm. After achieving a base pressure of 5×10^{-5} mbar, ultrapure (99.999%) argon gas was introduced with a flow rate of 27.4 sccm and the work pressure was maintained at 5×10^{-2} mbar during sputtering. The films were deposited at room temperature (RT) by varying the DC power such as 50, 100, and 150 W and by altering the pulsing frequency, namely, 25, 50, and 100 kHz.

The electrochromic properties of WO_3 films were studied by cyclic voltammetry technique using electrochemical analyzer/workstation (CH Instruments Inc., USA; Model: 604D) with a standard three-electrode configuration consisting of the sample ($\text{WO}_3/\text{SnO}_2:\text{F}/\text{glass}$) as the working electrode,

Ag/AgCl as a reference electrode, and Pt counter electrode. Pulsing frequency and DC power induced changes in optical property of coloured and bleached WO_3 films were measured by using a UV-Visible-NIR spectrophotometer (Ocean Optics HR 2000) in the wavelength range of 300–1000 nm.

3. Results and Discussion

The electrochromic behaviour of pulsed DC magnetron sputtered WO_3 film was tested by intercalating/deintercalating H^+ ions through three-electrode electrochemical cell using an electrolyte containing 0.1 M H_2SO_4 electrolyte solutions. The ion intercalation (i.e., coloration) and deintercalation (i.e., bleaching) processes were noted during the cycling of different scan rates, like 50, 100, and 150 mV/s. The current resulting from these scan rates is cathodic spike current (i_{pc}), which is associated with the coloring process of the film, and the anodic peak current (i_{pa}) is associated with

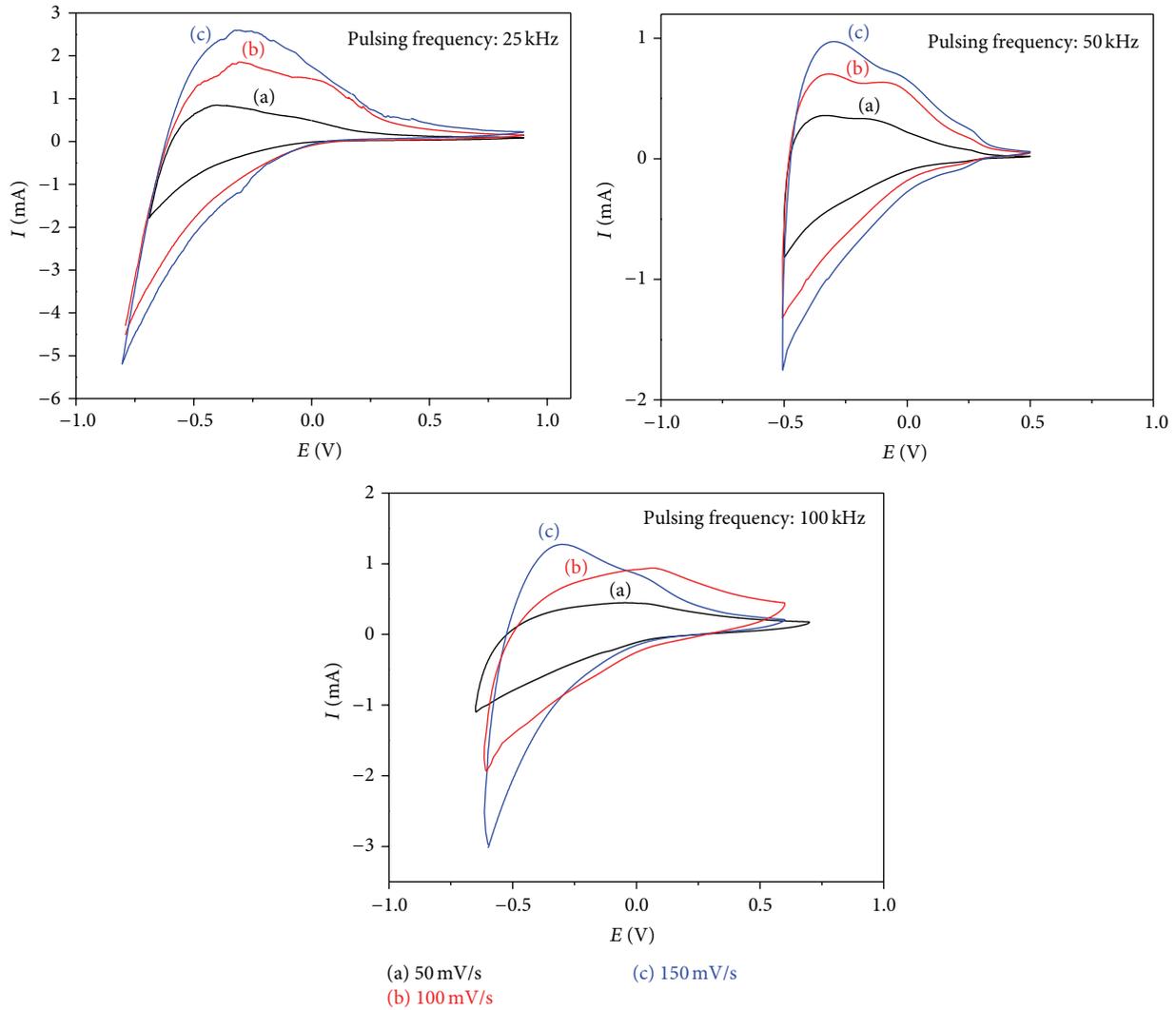


FIGURE 3: Pulsing frequency induced change in cyclic voltammograms of WO_3 films deposited at 150 W DC power and cycled in 0.1 M H_2SO_4 electrolyte solution with various scan rates.

the bleaching process. The cyclic voltammograms of the films were recorded in the potential range from -1.0 to $+1.0$ V. During the intercalation of the ion, that is, in negative potential of the scan, the films have changed their colour into dark blue (at -1.0 V) and returned to their original colour in the positive potential, that is, while the deintercalation of ions (at $+1.0$ V). This is attributed mainly to the electrochemical process involved in the reaction represented by the formation of “tungsten bronze” according to (1). The clearly observed colouration \leftrightarrow bleaching mechanism of pulsed DC magnetron sputtered WO_3 films confirmed the perfect electrochromic nature of the films associated with the electrochemical intercalation and deintercalation of H^+ ions and electrons into WO_3 lattice, which emphasized its suitability in electrochromic devices. Figures 1, 2, and 3 show the pulsing frequency induced variation in cyclic voltammograms of WO_3 films cycled in 0.1 M H_2SO_4 electrolyte solution deposited at various DC powers of 50, 100, and

150 W, respectively. Each sample was cycled at different scan rates such as 50, 100, and 150 mV/s. It is observed from Figures 1–3 that the magnitudes of both anodic peak current and cathodic spike current increase with the increasing scan rates and DC power (during film preparation), which revealed that the intercalation/deintercalation of H^+ ions is enhanced with the increasing DC power and scan rates. Thus, the WO_3 films can be reversibly made transparent by electrochemical oxidation and colored by reduction in a proton containing solution according to (1).

The extent of the intercalated and deintercalated H^+ ions can be studied by calculating the effective diffusion coefficient (D) by Randle-Sevcik equation [1]:

$$i_p = 2.72 \times 10^5 \times n^{3/2} \times D^{1/2} \times C_0 \times v^{1/2}, \quad (2)$$

where i_p is the peak current (i_{pc} and i_{pa}), D is the diffusion coefficient, C_0 is the concentration of active metal ions in

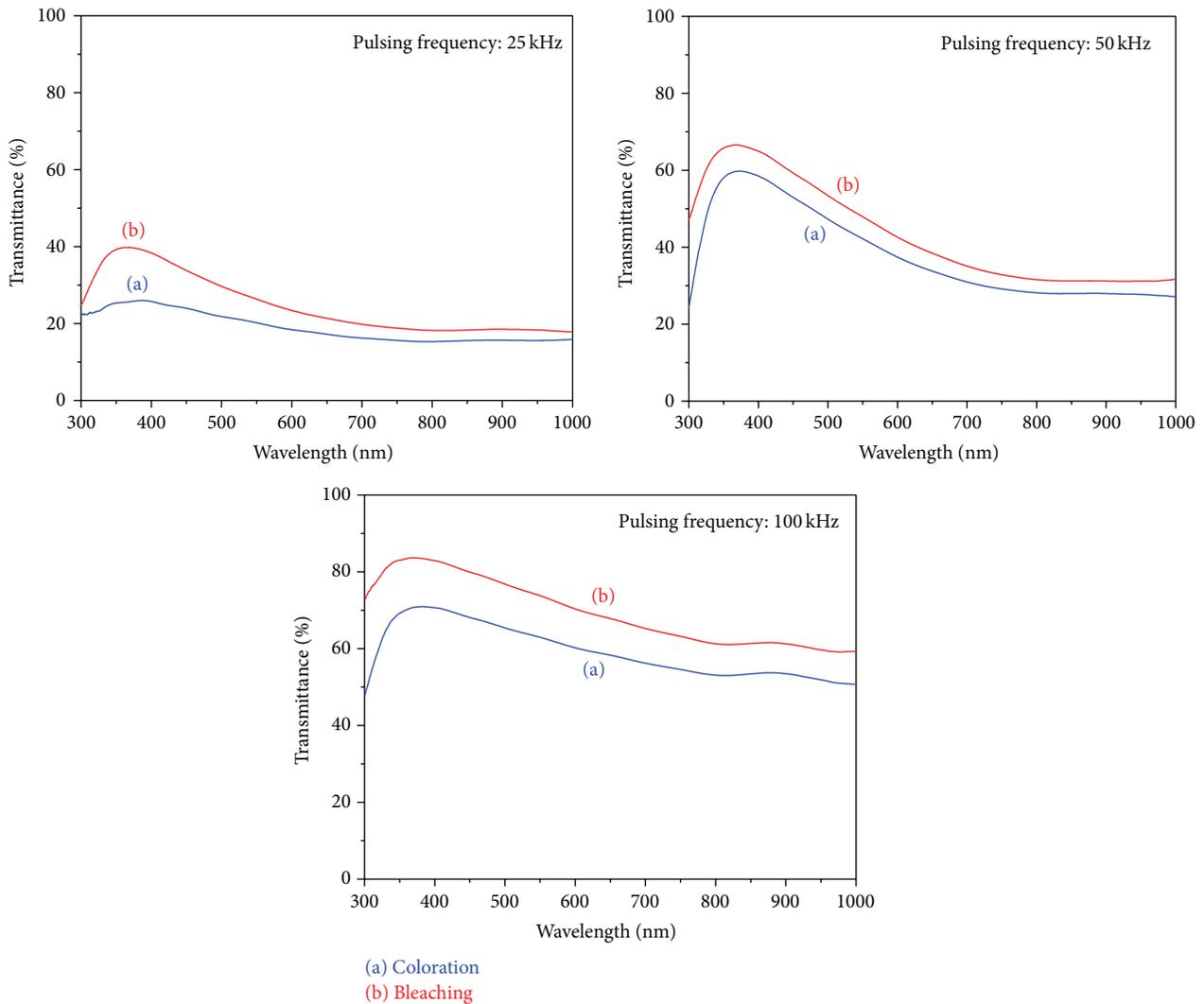


FIGURE 4: Optical transmittance spectra of coloured and bleached WO_3 thin films deposited at 50 W DC power and cycled in 0.1 M H_2SO_4 electrolyte solution.

the electrolyte, ν is the scan rate, and $n = 1$ is the number of electrons involved in the process. Table 1 shows the DC power, pulsing frequency, and scan rate induced variations in peak current and diffusion coefficient values of WO_3 films cycled in 0.1 M H_2SO_4 electrolyte solution. It is observed that the diffusion coefficient varies from 3.73×10^{-13} to 5.48×10^{-9} cm^2/s . It can be mentioned that Patil et al. reported that the diffusion coefficient of WO_3 films cycled in H_2SO_4 electrolyte is of the order of 10^{-10} cm^2/s [19]. In addition, they have suggested that the D values of WO_3 films vary in the range from 1×10^{-9} to 21×10^{-12} cm^2/s , depending on the preparation technique of the films [19]. Hence, the evaluated diffusion coefficient values in the present work are in accordance with reported values [19, 20].

The changes in optical transmittances of colored and bleached WO_3 films cycled in 0.1 M H_2SO_4 electrolyte solution were studied by UV-Vis-NIR spectrophotometer and the corresponding transmittance spectra are shown in Figures 4, 5, and 6 for the films deposited at various DC powers such

as 50, 100, and 150 W, respectively. The insertion of H^+ ions changes the transmittance from near ultraviolet up to the near infrared range and the reversible colour of the film from transparent to blue. In addition, the observed optical transmittance spectra possess higher optical modulation in the visible region and lower optical modulation in the infrared region. This can be attributed to the maximum optical absorption of WO_3 films in their intercalation and deintercalation process in the visible range. From these marked variations between the transmittance spectra of coloured and bleached states, it is observed that all the films show good electrochromic colouration. The transmittance in the visible range has been found to be significantly different for the films in bleached and coloured states though the shape has no apparent change. This effect could make them useful in electrochromic device and smart window applications. In order to have better insight into the role of pulsed DC magnetron sputtered WO_3 films in electrochromic device applications, we have attempted to evaluate the optical

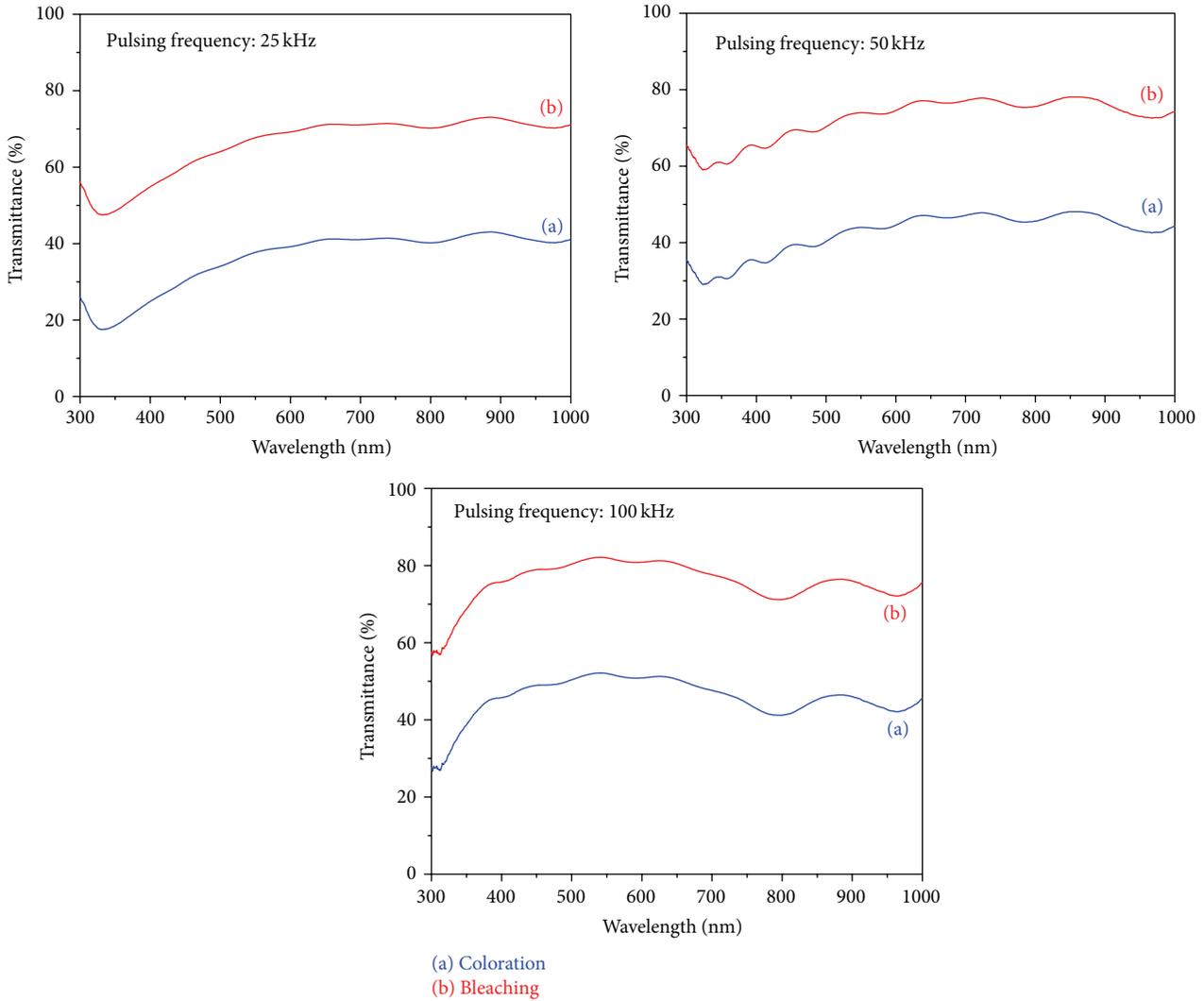


FIGURE 5: Optical transmittance spectra of coloured and bleached WO_3 thin films deposited at 100 W DC power and cycled in 0.1 M H_2SO_4 electrolyte solution.

density (OD) and colouration efficiency (CE) of the films from transmittance spectrophotometry using the formula [21, 22]

$$\text{OD}_{(\lambda=633\text{ nm})} = \log \left(\frac{T_b(\lambda=633\text{ nm})}{T_c(\lambda=633\text{ nm})} \right), \quad (3)$$

where T_b and T_c are the bleached and coloured transmittance, respectively. The coloration efficiency is given by

$$\text{CE} = \frac{\text{OD}}{Q_{\text{in}}}, \quad (4)$$

where Q_{in} (mC/cm^2) is the charge injected during the coloration cycle. Generally, tungsten oxide is known to have optical absorption maximum closer to the human eye sensitivity maximum. Hence, we would like to study spectral transmittance of WO_3 films in the visible region ($\lambda = 633\text{ nm}$). Table 2 shows the evaluated OD and CE values

of pulsed DC sputtered WO_3 films as a function of DC power and pulsing frequency. It is seen that the evaluated optical density varies between 0.056 and 0.211 and the colouration efficiency lies in the range of 37 to 79 cm^2/C . The colouration efficiency of the films increased with increasing DC power during film preparation. However, for a particular DC power, the CE was reduced with increasing pulsing frequency and the maximum colouration efficiency of 79 cm^2/C was observed for the film deposited at DC power of 150 W and pulsing frequency of 25 kHz. As mentioned above, the electrochromic performance of WO_3 film depends on the crystal structure and morphology. If the film is less dense, the metal ions are easily injected and extracted from the film surface and these films can possess a better performance in the electrochromic studies [1]. Hence, in the present work, the electrochromic response of pulsed DC sputtered WO_3 films is strongly influenced by the pulsing frequency and DC power which in turn decide the structure and morphology

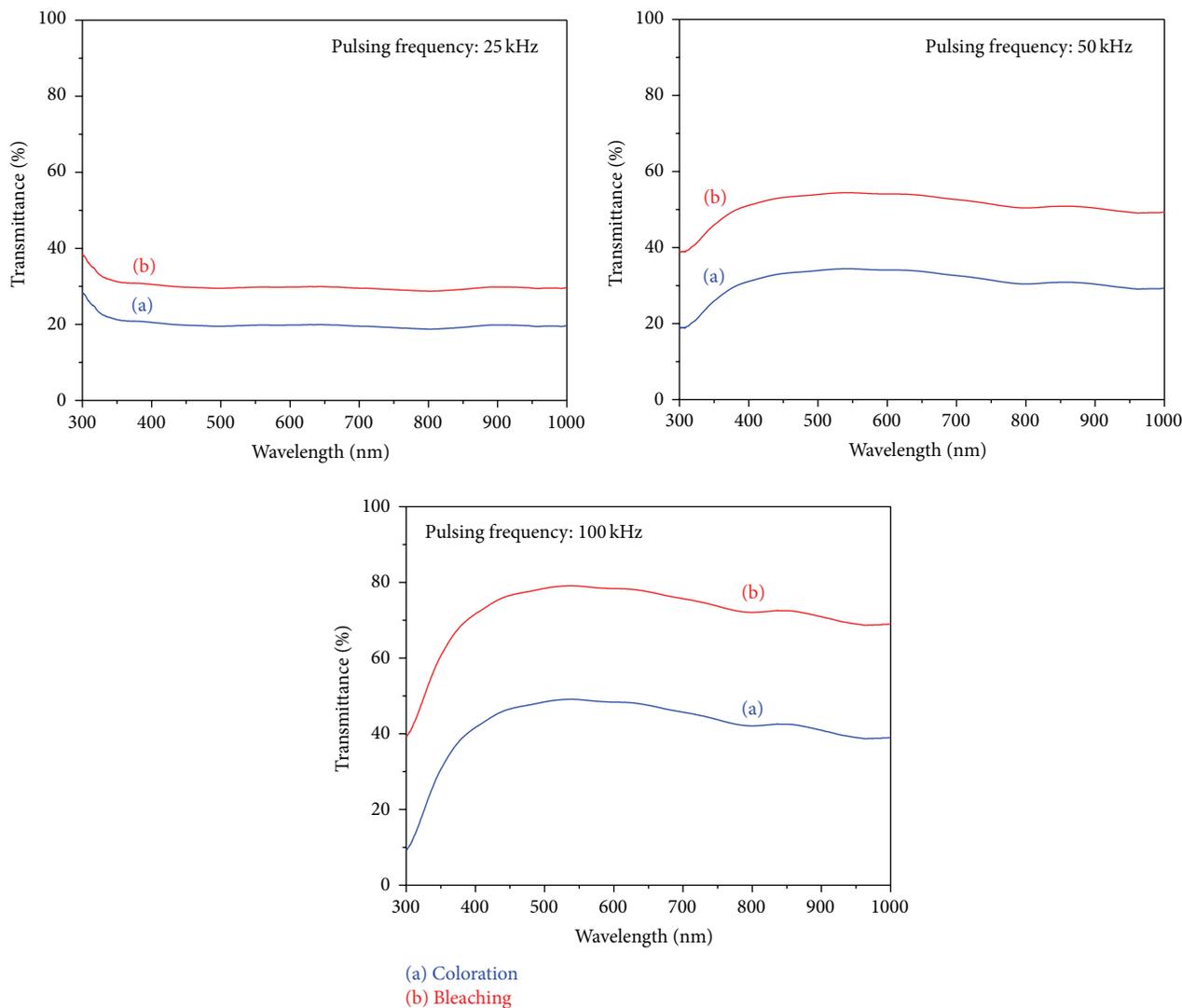


FIGURE 6: Optical transmittance spectra of coloured and bleached WO_3 thin films deposited at 150 W DC power and cycled in 0.1 M H_2SO_4 electrolyte solution.

of the deposited films. Several authors have reported the electrochromic properties WO_3 films deposited by different techniques and cycled in various electrolyte solutions. For instance, Patil et al. reported that the colouration efficiency of spray deposited WO_3 films varies between 40 and 56 cm^2/C [19]. In our earlier work, we have observed the colouration efficiency of 8 to 32 cm^2/C for the electron beam evaporated WO_3 films cycled in 0.1 M H_2SO_4 electrolyte solution [23]. In addition, we have reported the maximum colouration efficiencies of 12 cm^2/C and 15 cm^2/C (at 633 nm) for the electron beam evaporated WO_3 films cycled in 0.1 M KCl and 0.1 M $\text{LiClO}_4 \cdot \text{PC}$ electrolyte solutions, respectively [24]. Further, Sun et al. [18] observed the maximum colouration efficiency of 42 cm^2/C at 633 nm for the Li^+ ion ($\text{LiClO}_4 \cdot \text{PC}$ electrolyte solution) intercalated reactive dc pulse sputtered WO_3 films. Kitao et al. [25] reported the highest colouration efficiency of 60 cm^2/C at 600 nm for the film prepared at the substrate temperature of 60°C. Based on the literature,

to the best of our knowledge, the colouration efficiency of 79 cm^2/C observed in the present work is the highest one for any WO_3 film cycled in H_2SO_4 electrolyte solution.

4. Conclusions

In summary, this paper describes the pulsing frequency and DC power induced changes in electrochromic properties of pulsed DC magnetron sputtered WO_3 films by intercalating/deintercalating H^+ ions using three-electrode electrochemical cell configuration. The colouration \leftrightarrow bleaching mechanism of WO_3 films confirm the perfect electrochromic nature of the films associated with the electrochemical insertion and extraction of H^+ ions and electrons into WO_3 lattice. The optical transmittance in the visible range has been found to be significantly different for the WO_3 films in bleached and coloured states, which could be useful in

TABLE 1: Various electrochemical parameters of WO₃ films cycled in 0.1 M H₂SO₄ electrolyte.

Film preparation conditions (DC power and pulsing frequency)	Scan rate (mV/s)	i_{pc} (mA)	$D(i_{pc})$ (cm ² /s)	i_{pa} (mA)	$D(i_{pa})$ (cm ² /s)
50 W; 25 kHz	50	0.93	2.37×10^{-10}	0.37	3.87×10^{-11}
	100	1.81	4.47×10^{-10}	0.75	7.60×10^{-11}
	150	2.54	5.82×10^{-10}	1.08	1.06×10^{-10}
50 W; 50 kHz	50	1.52	6.28×10^{-10}	0.52	7.34×10^{-11}
	100	3.45	1.61×10^{-9}	1.38	2.59×10^{-10}
	150	5.17	2.41×10^{-9}	2.11	4.04×10^{-10}
50 W; 100 kHz	50	1.42	5.48×10^{-9}	0.61	1.02×10^{-10}
	100	3.46	1.62×10^{-9}	1.37	2.54×10^{-10}
	150	3.87	1.35×10^{-9}	1.55	2.18×10^{-10}
100 W; 25 kHz	50	0.77	1.62×10^{-10}	0.08	1.93×10^{-12}
	100	2.04	5.64×10^{-10}	0.73	7.39×10^{-11}
	150	6.08	3.33×10^{-9}	2.05	3.80×10^{-10}
100 W; 50 kHz	50	0.94	2.39×10^{-10}	0.03	3.73×10^{-13}
	100	1.27	2.19×10^{-10}	0.33	1.55×10^{-11}
	150	1.99	3.60×10^{-10}	0.89	7.26×10^{-11}
100 W; 100 kHz	50	2.27	1.40×10^{-9}	0.84	1.91×10^{-10}
	100	4.06	2.23×10^{-9}	1.66	3.73×10^{-10}
	150	5.03	2.28×10^{-9}	2.29	4.75×10^{-10}
150 W; 25 kHz	50	1.82	8.99×10^{-10}	0.85	1.95×10^{-10}
	100	4.22	2.41×10^{-9}	1.85	4.64×10^{-10}
	150	5.15	2.39×10^{-9}	2.59	6.07×10^{-10}
150 W; 50 kHz	50	0.83	1.87×10^{-10}	0.37	3.72×10^{-11}
	100	1.32	2.37×10^{-10}	0.71	6.81×10^{-11}
	150	1.73	2.70×10^{-10}	0.98	8.70×10^{-11}
150 W; 100 kHz	50	1.08	3.15×10^{-10}	0.45	5.60×10^{-11}
	100	1.91	4.96×10^{-10}	0.95	1.23×10^{-10}
	150	2.99	8.09×10^{-10}	1.28	1.49×10^{-10}

TABLE 2: Optical density (OD) and coloration efficiency (CE) of WO₃ films (at $\lambda = 633$ nm) cycled in 0.1 M H₂SO₄ electrolyte solution.

DC power (W)	Pulsing frequency (kHz)	OD	CE (cm ² /C)
50	25	0.095	52
	50	0.056	44
	100	0.066	37
100	25	0.240	59
	50	0.210	56
	100	0.200	49
150	25	0.176	79
	50	0.201	64
	150	0.211	56

electrochromic device and smart window applications. The maximum coloration efficiency of 79 cm²/C was obtained for the film deposited at 150 W and pulsing frequency of 25 kHz. Hence, it may be concluded that the pulsed DC magnetron sputtering can be used as a potential technique to

grow device quality WO₃ films with superior electrochromic performance.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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